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Introductory Chapter: Microemulsions

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1. Introduction

An emulsion is a dispersion of droplets of one liquid in a second immiscible liquid. The droplets are termed the dispersed phase, while the second liquid is the continuous phase. To stabilize an emulsion, a surfactant or co-surfactant is added such that the droplets remain dispersed and do not separate out as two phases. Depending on the phase, there are two types of microemulsions: water-in-oil (w/o) and oil-in-water (o/w). As the name implies, water is the dispersed phase in w/o emulsions, whereas oil is the dispersed phase in o/w emulsions [1, 2]. One of the main differences between macroemulsions and microemulsions is that the size of the droplets of the dispersed phase of microemulsions is between 5 and 100 nm, while that of macroemulsions is >100 nm. Microemulsions are thermodynamically stable systems, whereas macroemulsions are kinetically stable systems [2]. Also, microemulsions are translucent and of low viscosity, while macroemulsions are opaque and of relatively high viscosity. Due to these unique properties of microemulsions, these systems have become indispensable in numerous important fields.

2. Characterization

Microemulsions, at the molecular scale, are a finely balanced system where the energetics of entropy and surface energies are opposing each other. The entropy of the system is increased by having a higher number of droplets dispersed, while the surface areas, and correspondingly surface energies are increased with more droplets. Slight changes in the chemical composition or conditions can shift this balance and may, therefore, lead to dramatic changes in the behavior of the system.

The expansion and integration of microemulsions into various applications (see Section 3) have imbued microemulsions with industrial and commercial importance. To optimize formulations and predictive models, adequate characterization is essential. Because microemul-

sions are essentially a subset of the broader class of emulsions, techniques which pertain to general emulsions also play a part in this regime. However, techniques which are specific to microemulsions have also emerged.

2.1. Phase behavior

Characterization of microemulsions necessarily begins with the elucidation of the phase behavior, where, in the most simple form, oil, water, and surfactant are mixed in different molar ratios, and the formed phases are tracked [3]. A generic phase diagram resulting from such analysis is shown in **Figure 1**. In several regions of the phase diagram, single phases exist in one end where spherical oil droplets are dispersed in water (o/w emulsions) and the other where spherical water droplets are dispersed in oil (w/o emulsions). Between these two extremes, depending on the ratio of components, the droplet shapes may change from spherical to cylindrical, to worm-like micelle, to bicontinuous [4]. Traditionally methods of microscopy, rheology, conductivity, and nephelometry have been used in the study of microemulsions, while instrumental techniques such as dynamic light scattering, neutron scattering, X-ray scattering, electron micrography, nuclear magnetic resonance, electron paramagnetic resonance, and their derivatives are widely used at present. Although detailed treatise of these myriad techniques is outside of the scope of this chapter; here, we briefly discuss the physical properties important to characterize microemulsions, and the techniques able to quantify them.

The phase behavior of the system can be characterized by several techniques. Other than using visual inspection, optical microscopy using polarized light is commonly used [5] to detect the presence of a singular phase, or the presence of separate phases. Simple electrical conductivity (EC) measurements can be used to identify whether the oil/water or both phases are continuous [5, 6]. The EC of a w/o emulsion increases with the addition of water. After the maximum amount of water that water in oil emulsion can hold is exceeded, the emulsion col-

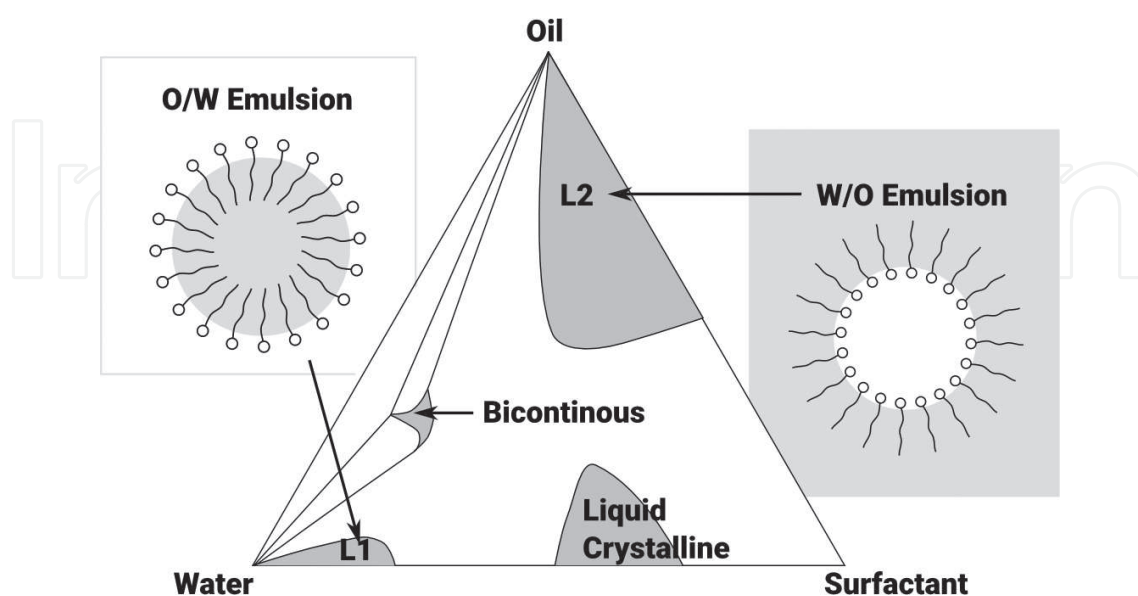


Figure 1. Example of a ternary phase diagram of oil/water/surfactant system. Here, the formation of oil-in-water (o/w) emulsions or water-in-oil (w/o) emulsions is determined by the molar ratio of the components. Adapted from Archarya et al. [3].

lapses and the EC decreases. On the other hand, for o/w emulsions, the EC is steady until the concentration of oil droplets increases and an effectively infinite conductive pathway arises leading to dramatic increases in measurements [6]. Microscopic techniques such as scanning electron microscopy (SEM) or transmission electron microscopy (TEM) have adequate resolution to image individual droplets or the morphology of a larger region. However, dehydration required for conventional sample preparation can severely affect the native structure [3, 7, 8].

2.2. Droplet size

Apart from the existence of the unitary phase, the size of droplets of the dispersed phase of a microemulsion is a primary characteristic, since it determines much of the physical behavior and functionality. Conventionally, the term, 'microemulsion' refers to a thermodynamically stable, isotropic emulsion with a droplet size of 1–100 nm. For macroemulsions, both sound (acoustics, electroacoustics) and visible light (turbidimetry, nephelometry, laser diffraction) can be used to characterize the droplet size. However, for emulsions of which the droplet size is less than 1 μ , the intensity of acoustic attenuation and diffuse light scattering decreases with droplet size. This leads to a useful property that microemulsions are not only transparent but also requires different techniques to characterize them.

In the domain of microemulsions, size (and shape) dependant scattering of visible light, X-Rays, electrons, and neutrons can be interrogated to yield useful information. Dynamic light scattering (DLS or PCS) is a widely used for characterizing particle size and shape anisotropy [3]. Here, the measurement is the fluctuation of scattered laser light intensity, which is related to the Brownian motion of particles (droplets) in the medium. Fitting the autocorrelation of the scattered light intensity to models of particles in specific media can lead to determining the diffusion constant, particle size distribution, and in some cases, shape anisotropy [9–11].

In the case of X-rays, because oil and water scatter X-rays to different extents, small angle X-ray scattering (SAXS) can also be used to obtain the size of the dispersed phase [3, 12]. Neutrons can also be used as the primary beam, and the variation in scattering intensity by different nuclei gives rise to small-angle neutron scattering (SANS). SANS data give access to both the droplet size and dynamic properties; however, the relative cost and data collection time limit the applicability of this technique [3].

Apart from scattering techniques, nuclear magnetic resonance (NMR) and related techniques are widely used in the characterization of microemulsions [3, 13]. Here, both relaxation [14] and self-diffusion experiments [15] are used to probe the emulsion systems [13, 16].

2.3. Droplet size distribution

It follows that most techniques which give a measure of the droplet size of microemulsions will also have access to the size distribution or polydispersity. Scattering techniques such as DLS, time-averaged light scattering, and SANS can characterize size distribution. However, due to the confluence of particle size variation and shape anisotropy, analyzing, and deconvoluting, these data may not always be straightforward. SANS is particularly versatile and can characterize the structure, and interactions of colloidal systems with a wide range of interactions as well as differences in orientation and droplets with non-spherical shapes [17].

2.4. Diffusion constant

Similarly, because most techniques use the motion of aggregates (droplets) to elucidate the sizes of dispersed droplets, light scattering techniques have access to the diffusion rates as well. However, it is important to note that fluorescence correlation spectroscopy (FCS) [3] can be used to measure the diffusion constants (in addition to particle size and size distribution [18]), particularly useful in dilute solutions and other conditions where light scattering techniques fail [3]. However, when the droplet sizes of the emulsions become comparable to the incident beam focus size, the FCS is not reliable leading to the technique being used as a complementary method to DLS [3].

Nuclear magnetic resonance and derivatives of the technique can be used to measure the self-diffusion constants of oil, water and the surfactants in microemulsions [3]. Microemulsion structure is best investigated by NMR relaxation and self-diffusion studies. Bicontinuity in equilibrium microemulsions can be obtained by self-diffusion studies. NMR relaxation is very sensitive to the droplet size but is insensitive to interactions allowing accurate droplet size measurements [13].

2.5. Morphology

Although all of the techniques discussed so far give information about the morphology, electron microscopy provides a robust method to directly visualize the nanoscale structure and morphology of microemulsions. For conventional TEM images, a thin ($\sim 10^2$ nm) specimen is required, while for SEM, deposition and fixation on a solid substrate are usually required. In each of these cases, the sample preparation requires dehydration which, in the case of microemulsions, can severely affect their native structure [3]. To alleviate this problem, cryo-electron microscopy (cryo-EM) techniques have been utilized where emulsions are frozen in their native hydrated states. From this point, preparing samples through freeze-fracture or freeze-etching [7, 8] can reveal rich and unique insight into the systems.

2.6. Rheology

The rheological properties of microemulsions are often crucial in their application because they will affect the processability, and kinetics, and stability under various conditions [19]. Microemulsions show varying rheology depending on the phase point. For example, o/w and w/o microemulsions show Newtonian behavior over a wide range of shears, while the bicontinuous phase may undergo breakage upon medium shear forces, leading to thinning [3]. Although the effect of the molecular structure of emulsions has a large impact on the behavior of microemulsions [20], the characterization techniques are generally the same as their macroscopic counterparts [21, 22].

3. Applications

The applications of microemulsions are plenteous and span in areas including drug delivery, cosmetics, food, fuel, lubricants and coatings, detergents, agrochemicals, analytical chemistry,

nanoparticle synthesis, biotechnology, and chemical reactors [23]. Exhibiting a pseudo biphasic behavior, these systems allow solubilization of highly hydrophilic substances in oil-based systems and highly hydrophobic substances in water-based systems. Further, ultralow interfacial tension, the presence of nanosized droplets of dispersed phase, slow release and protection of encapsulated material, and the ability to penetrate through biological membranes are some attributes that make the microemulsions find significant applications in various sectors. A brief description of the applications of microemulsions in selected fields is given below.

3.1. Pharmaceuticals

Emulsions are opaque gels or creams in which a drug is dispersed for topical application. The effect of the drug released from the gel depends on the permeability of the drug through the skin barrier. Microemulsions considering the small size of the droplets can serve as better delivery vehicles thereby improving the drug solubility, penetrability, and shelf life [24]. An advantage of these systems is their ability to deliver both hydrophobic and hydrophilic drugs efficiently via o/w or w/o emulsions, respectively [25]. It has been shown that penetrability of hydrophobic drugs is improved by encasing the drug in a lipid vesicle [26]. Therefore, it is apparent that the smaller the size of the droplet, the better the delivery of a hydrophobic drug. Drug diffusion was shown to follow kinetics related to models such as Higuchi model resulting in the slow release of the drug [27]. In this case, the permeation was shown to increase when glycolipids were incorporated into the microemulsion indicating that they could outperform macroemulsions in topical drug delivery. Poorly soluble drugs such as cyclosporine and paclitaxel have shown improved oral bioavailability in microemulsion systems and have been patented along with other drugs such as ritonavir and saquinavir [28].

3.2. Cosmetics

Cosmetics and cosmeceutics currently utilize microemulsion systems and demonstrate the enormous potential of using these systems for various products. Skin care products, hair care products, and perfumes are the main types of microemulsion products available in the market. The surfactants, co-surfactants, and oils used in cosmetic microemulsions are either natural or synthetic. The surfactants are either ionic or nonionic [23]. Bioactive agents, including antioxidants and skin whitening agents, have been incorporated in and delivered to the skin via microemulsion cosmetic products [29, 30]. Interestingly, antioxidant and moisturizing effects of olive oil, which can be utilized as the main ingredient in microemulsions, increase upon incorporation in microemulsions thus making such systems apt for cosmetic applications [31]. In addition to delivering nutrients and increasing moisturizing effects, microemulsions have been identified as promising systems for removing oily make-up cosmetics from the skin [32].

3.3. Food

Numerous attributes of microemulsions render these systems excellent to be used in the food sector. Among such attributes, their ability to protect, slowly release, and enhance the activity of the encapsulated material, and the possibility of formulating microemulsions using edible substances, stand out. According to a recent study, garlic essential oils encapsulated in water-based microemulsions have exhibited antimicrobial activity indicating its potential use in the

food industry [33]. Further, the bioactive compounds—crocin, safranal, and picrocrocin—of saffron encapsulated in multiple emulsions have shown enhanced slow release properties and greater stability in gastric conditions [34]. Moreover, microemulsions encapsulating steppogenin have shown to be effective in reducing enzymatic browning of apple juice. Co-encapsulation of vitamin C with steppogenin greatly enhances this antibrowning effect [35]. The number of studies on applications of microemulsions in food is plentiful and is still growing.

3.4. Enhanced oil recovery

Microemulsions are used in enhanced oil recovery, and approximately 20% enhanced oil recovery has been reported. The high interfacial tension between the crude oil and reservoir brine keeps the residual oil in the reservoir. The interfacial tension can be lowered via the preparation or introduction of microemulsions, and thus, this area is actively investigated. A surfactant formulation is injected into the reservoir in the surfactant-polymer flooding process. The surfactants stimulate the formation of a microemulsion in the porous reservoir between reservoir brine and crude oil, which reduces the interfacial tension between the two. Hence, the oil recovery is enhanced [36]. A more recent trend is to utilize more cost-effective microbes to produce microbial products including biosurfactants in place of chemical mixtures [37, 38]. Also, numerous studies have been conducted to evaluate the use of ionic liquids as green chemicals in place of surfactants in microemulsions in enhancing oil recovery [39].

3.5. Fuels

Microemulsions have been used as fuels with many attractive properties. These fuels are used to decrease the emission rates of gases such as nitrogen oxides and carbon monoxide, and particles (soot) [40]. Although alcohols frequently used in microemulsion biofuels decrease the cetane number. The incorporation of cetane improvers has significantly increased the cetane number thus improving the properties of microemulsion fuels [41]. Moreover, water in the microemulsion-based fuel reduces the combustion temperature and heat released. Due to the increased surface area, the air-fuel contact is improved. Overall, the fuel efficiency is improved as microemulsion-based fuels are used [42].

3.6. Lubricants, cutting oils and corrosion inhibitors

Microemulsion systems are frequently used as lubricants. Microemulsions prepared using ionic liquids and copper nanoparticles are some recent advances in this field [43, 44]. As cutting oils, microemulsions serve as lubricants and absorbers of the heat of friction [45]. As corrosion inhibitors, microemulsions may show many mechanisms of action. The corrosion causing factors may be soluble in the microemulsion so that those factors may be unavailable for the metal surface. Also, the hydrophobic coating on the metal may prevent corrosion [46].

3.7. Coatings and textile finishing

Microemulsion-based resins exhibit superior properties than solvent-based resins. Mainly, flammability hazards, health problems, and pollution problems are much less associated

with microemulsion-based coatings. Further, microemulsion coatings are better than emulsion coatings with respect to scrub resistance, stain resistance and color intensity [23, 47, 48]. The suitability of microemulsions in textile finishing has also been demonstrated by many researchers. In fact, microemulsions have shown better properties than both conventional textiles finishing aids and normal emulsions [23, 49].

3.8. Nanoparticle synthesis

Microemulsions have been commonly used as means of preparing nanoparticles. Recently, bimetallic nanocatalysts comprising Cu and Ni were formed using reserved microemulsions where they altered the microemulsion composition to obtain different sizes of bimetallic particles [50]. Narrow size distribution and regular shape are two other important attributes of metallic nanoparticles synthesized using the reversed microemulsion method [51–53]. In addition to inorganic nanoparticles, organic nanoparticles such as cholesterol and rhovanil have been prepared successfully using microemulsions. Also, the properties of nanoparticles may, in certain instances, be modulated by changing the physicochemical properties of microemulsions [54].

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